

# THE EFFICIENCY OF ORGANIC SCINTILLATORS

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## 1. INTRODUCTION.

There are four main types of organic scintillator:

- (a) pure crystals, e.g. anthracene;
- (b) mixed crystal solid solutions, e.g. anthracene in naphthalene;
- (c) liquid solutions, e.g. *p*-terphenyl in toluene; and
- (d) plastic solutions, e.g. *p*-terphenyl in polystyrene.

Except in pure crystals there are always at least two components present, the solvent and the primary solute. The solute concentration is generally small, so that practically all the incident energy of the ionizing radiation is expended in the excitation and ionization of the solvent molecules. A fraction of the resultant solvent excitation energy is then transferred to the solute molecules, and the fluorescence emission of the solute forms the scintillation normally detected by the photomultiplier. In many liquid and plastic solution scintillators secondary solutes, e.g. POPOP, are added to shift the primary solute spectrum to match more closely the photomultiplier spectral response. In such

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systems an additional stage of inter-molecular energy transfer, from primary to secondary solute, is involved.

## 2. THE PRIMARY PROCESSES.

In the present paper it is proposed to discuss the factors determining the scintillation efficiency of the various types of organic scintillator. The primary events associated with the initial excitation and ionization of the solvent molecules by the ionizing radiation have been discussed more fully elsewhere (1). The alternative primary processes may be summarized as follows:

- (1) excitation into excited  $\pi$ -electron singlet states;
- (2)  $\pi$ -electron ionization;
- (3) excitation of other ( $\sigma$ -electron) excited states;  
and
- (4) ionization of electrons other than  $\pi$ 's.

Process 1 is the origin of the main fast scintillation emission (decay time  $\sim 2-10$  nsec.) since only the de-excitation of the  $\pi$ -electron excited states results in fluorescence.

Ion recombination, following process 2, results in molecules in excited singlet or triplet  $\pi$ -states, and produces the slow scintillation component (decay time  $\sim 300$  nsec.) observed in many organic scintillators, in the absence of oxygen (2). The relatively long decay time of this component arises either from the ion recombination time (3) or from the lifetime of intermediate triplet states populated preferentially on ion recombination (1).

The excitation energy of non- $\pi$  excited states (process 3) is dissipated thermally and does not result in fluorescence. It is the major cause of the relatively low efficiency of the scintillation process compared with the photo-fluorescence process, where only  $\pi$ -electron states are excited by near ultra-violet radiation.

Process 4, ionization, leads to temporary and permanent molecular damage and to ion recombination. The temporary molecular damage associated with the ionization density along

the track of the ionizing particle is responsible for the ionization quenching effect observed in all organic scintillators (4), which reduces the scintillation efficiency for more heavily ionizing particles. The permanent molecular damage introduces quenching centers which cause a gradual decrease in fluorescence efficiency under prolonged intense irradiation (5). Ion recombination into non- $\pi$  excited states leads to thermal dissipation of the energy, as in process 3.

The relative probabilities of excitation and ionization in an organic molecule are approximately 2:1. If each electron in the molecule is considered to have the same total excitation and ionization cross-section, then the fraction of the incident energy expended in the excitation and ionization of  $\pi$  electrons (processes 1 and 2) can be evaluated from the fraction of  $\pi$ -electrons in the molecule. The results of this simple model, applied to several molecules of interest, are shown in Table 1.

A more sophisticated model would allow for differences in the excitation and ionization cross-sections of the  $\pi$ - and  $\sigma$ -electrons, and of the K-electrons in the C atoms. This might modify the absolute values of the probabilities, but it should not change their relative order which depends only on the fraction of  $\pi$ -electrons in the molecule.

The scintillation efficiency S for excitation by fast electrons is given by

$$S = PQ \quad (1)$$

where P is the efficiency of the primary  $\pi$ -excitation and Q is the efficiency of the subsequent processes by which the  $\pi$ -excitation energy is converted into fluorescence emission. According to the theoretical model

$$P = \frac{2}{3} \quad (\text{the } \pi\text{-electron fraction}) \quad (1a)$$

Q can be measured and studied using ultra-violet excitation directly into the  $\pi$ -singlet states, and by comparison with similar scintillation studies the primary and subsequent processes can be differentiated. Apart from the major survey of the pure crystal organic scintillators by Sangster and Irvine (6), who compared the relative values of S and Q and hence showed that P is approximately independent of the nature of the scintillator, most experimental studies have been concerned only with a comparison of the relative

TABLE 1

Molecule	No. of Electrons $\pi$	Total	Fraction of $\pi$ 's	$\pi$ -excitation probability P (Process 1)	$\pi$ -ionization probability (Process 2)
Anthracene	14	94	0.149	0.099	0.050
Quaterphenyl	24	162	0.148	0.099	0.049
Naphthalene	10	68	0.147	0.098	0.049
p-Terphenyl	18	122	0.147	0.098	0.049
Benzene	6	42	0.143	0.095	0.048
Polyvinyl-naphthalene	10n	82n	0.122	0.081	0.041
Polystyrene	6n	56n	0.107	0.071	0.036

magnitudes of S, or, in fewer cases, of Q or quantities related thereto. The similar values of P, the  $\pi$ -excitation probability, for the first 4 compounds in Table 1, confirm the experimental findings of Sangster and Irvine, and show that the differences in S for pure crystal scintillators are due mainly to differences in Q.

For crystalline anthracene it is estimated below that  $Q = 0.37$ , so that taking  $P = 0.099$  from Table 1,  $S = 0.037$ , which is in excellent agreement with the experimental value of  $S = 0.038$  obtained by Birks and Szendrei (7).

The relative magnitudes of the fast and slow components depend on the relative probabilities of  $\pi$ -excitation and  $\pi$ -ionization producing  $\pi$ -singlet states. Since statistically 0.25 of ion recombinations are into singlet states (3), the theoretical ration is 8:1 in reasonable agreement with the measurements of Owen (8) on several scintillators under fast electron (gamma-ray) excitation. With proton excitation the fast component is reduced due to ionization quenching (4), but the slow component associated with ion recombination is unquenched, thus accounting for the dependence of the fast-slow component ratio on the nature of the ionizing particle (8). This has been shown to be in quantitative agreement with the experimental data (1).

The higher value of P for benzene compared with those for the two polymers indicates why liquid solutions are generally more efficient scintillators than plastic solutions, with similar solutes for which the values of Q can be equated by optimum choice of concentration. Liquid solutions have a lower scintillation efficiency than anthracene crystals. As will be shown subsequently, this is due to a lower inherent value of Q, since the values of P are similar in the two cases. The increased value of P for polyvinyl-naphthalene compared with polystyrene indicates that improved plastic solvents can be evolved, by increasing the size of the aromatic ring substituent in the polyvinyl chain, thereby increasing the  $\pi$ -electron function.

### 3. THE SUBSEQUENT PROCESSES

#### 3.1. Internal Conversion.

The energies of the excited  $\pi$ -electron singlet states of an aromatic molecule can be obtained from its ultra-violet absorption spectrum. The transition moments from the singlet ground state ( $S_0$ ) to the different excited singlet states ( $S_1, S_2, S_3$ , etc.) are related to the magnitudes of the extinction coefficients in the absorption bands associated with each transition. In general it is found that the transition moments to the 2nd and 3rd excited singlet states ( $S_2$  and  $S_3$ ) are very much larger than to any of the other  $\pi$ -electron states, showing that the  $\pi$ -excitation by ionizing radiation is predominantly into  $S_2$  and  $S_3$ .

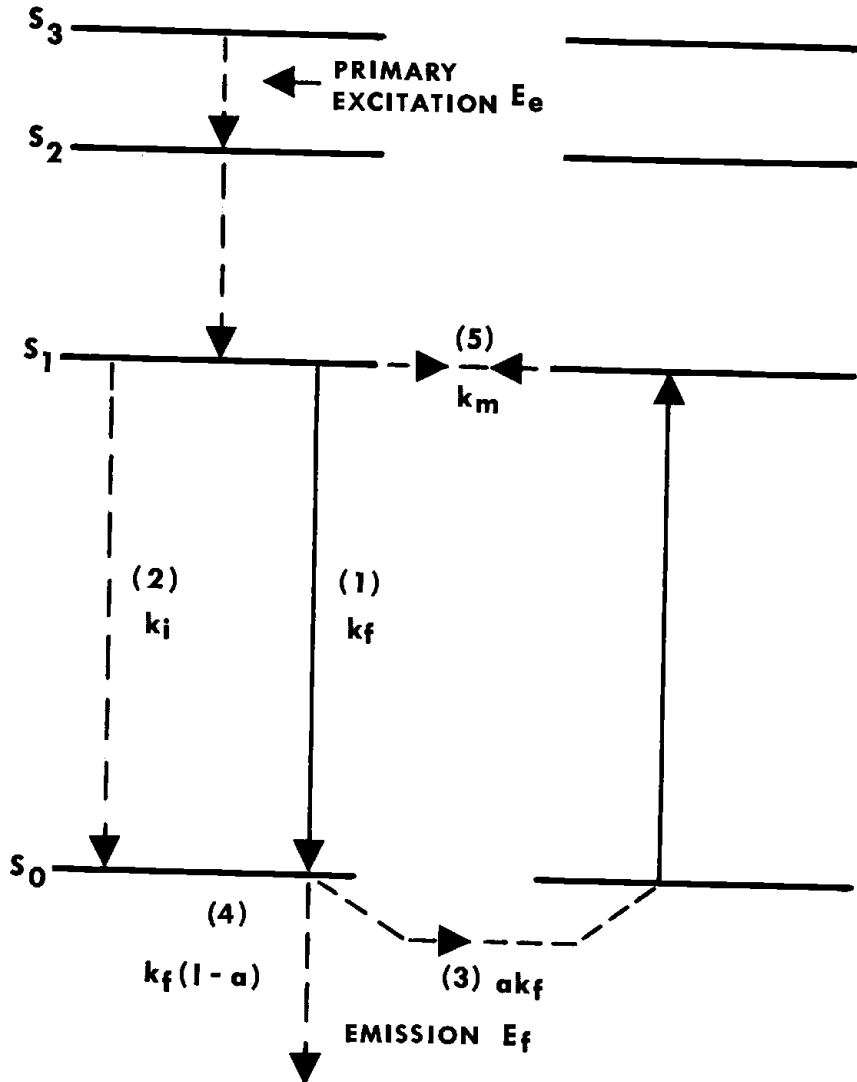
The fluorescence emission of the molecule normally occurs from the 1st excited singlet state  $S_1$ , and corresponds to the  $S_1 - S_0$  transition. Measurements on a number of organic fluors have shown that the quantum efficiency of fluorescence  $q_0$  is independent of whether the  $S_1, S_2$ , or  $S_3$  state is initially excited, provided no competitive processes such as photo-chemical dissociation, dimerization, or energy transfer from higher excited states occur. With this restriction, which appears to be valid for most organic scintillator molecules studied, it is thus seen that the primary  $S_2$  and  $S_3$  excitation energy is internally converted with 100 percent quantum efficiency into  $S_1$  excitation energy, the excess energy being dissipated as thermal vibrations to neighboring molecules (Figure 1).

#### 3.2. Pure Crystals.

The processes competing for the  $S_1$  excitation energy in a pure crystal scintillator and their relative probabilities

FIGURE 1

## ENERGY LEVELS, PROCESSES, and PROBABILITIES in pure CRYSTAL SCINTILLATOR



are as follows (Figure 1):

- (1) Emission,  $k_f$ , ending to processes (3) or (4);
- (2) Internal quenching,  $k_i$ ;
- (3) Radiative migration,  $ak_f$ ;
- (4) Escape of emission,  $(1 - a) k_f$ .

The absorption parameter  $a$  depends on the overlap of the emission and absorption spectra of the crystal and on the crystal thickness  $d$  (9). In anthracene at 290°K, for example,  $a = 0.82$  for  $d \geq 2$  mm. The additional process,

- (5) Non-radiative migration,  $k_m$

or exciton migration, which occurs with high efficiency in pure crystals does not affect the bulk crystal properties with which we are concerned here.

For  $a = 0$  (thin crystal) the molecular fluorescence quantum efficiency is

$$q_0 = \frac{k_f}{k_f + k_i} \quad (2)$$

The technical (thick specimen) fluorescence quantum efficiency (1,10) is reduced by self-absorption to

$$q_p = \frac{q_0(1 - a)}{1 - q_0 a} \quad (3)$$

The energy conversion efficiency  $Q$  from the primary excitation to the fluorescence emission of a pure crystal is

$$Q = \frac{E_f}{E_e} q_p = \frac{\lambda_e}{\lambda_f} q_p \quad (4)$$

where  $E_e$  and  $E_f$  are the mean energies of the primary excitation and the fluorescence emission respectively. These can be obtained from  $\lambda_e$  and  $\lambda_f$ , the mean wavelengths ("centers of gravity") of the absorption and emission spectra respectively.

For anthracene at 290°K,  $k_f = 1.4 \times 10^8 \text{ sec}^{-1}$ ,  $k_i =$

$1.6 \times 10^7 \text{ sec}^{-1}$ ,  $a = 0.82$  ( $d \geq 2 \text{ mm.}$ ),  $q_o = 0.9$  and  $q_p = 0.62$  (1). The crystalline anthracene spectrum below  $2,200 \text{ \AA}$  has not been reported, but it is estimated that  $\lambda_e = 2500 \text{ \AA}$ , and  $\lambda_f = 4200 \text{ \AA}$ , giving  $Q = 0.37$ . In conjunction with  $P = 0.099$  from Table 1, this yields  $S = 0.037$ , in agreement with the experimental value of  $S = 0.038$  (7).

### 3.3. Binary Solutions.

In the subsequent discussion we shall use X, Y and Z and corresponding suffixes to refer to molecules of the solvent, primary solute and secondary solute respectively. The quantities [Y] and [Z] represent concentrations of primary and secondary solutes respectively in moles/mole of solvent. The terms  $k_f$ ,  $k_i$ , and  $k_t[Y]$  with appropriate suffixes, are defined as rate parameters, corresponding to the probabilities (in  $\text{sec}^{-1}$ ) of emission, internal quenching and non-radiative transfer respectively. To simplify the discussion additional possible quenching processes, such as concentration quenching of the solute, external solute quenching of the solvent, and impurity (e.g. oxygen) quenching, will be omitted, although these can readily be included in a full formal treatment. The quantities  $a_{xx}$ ,  $a_{xy}$  and  $(1 - a_{xx} - a_{xy})$  are the fractions of the solvent emission absorbed by X, absorbed by Y, and escaping from the system respectively. The term  $a_{xx}$  corresponds to  $a$  in Section 3.2., while

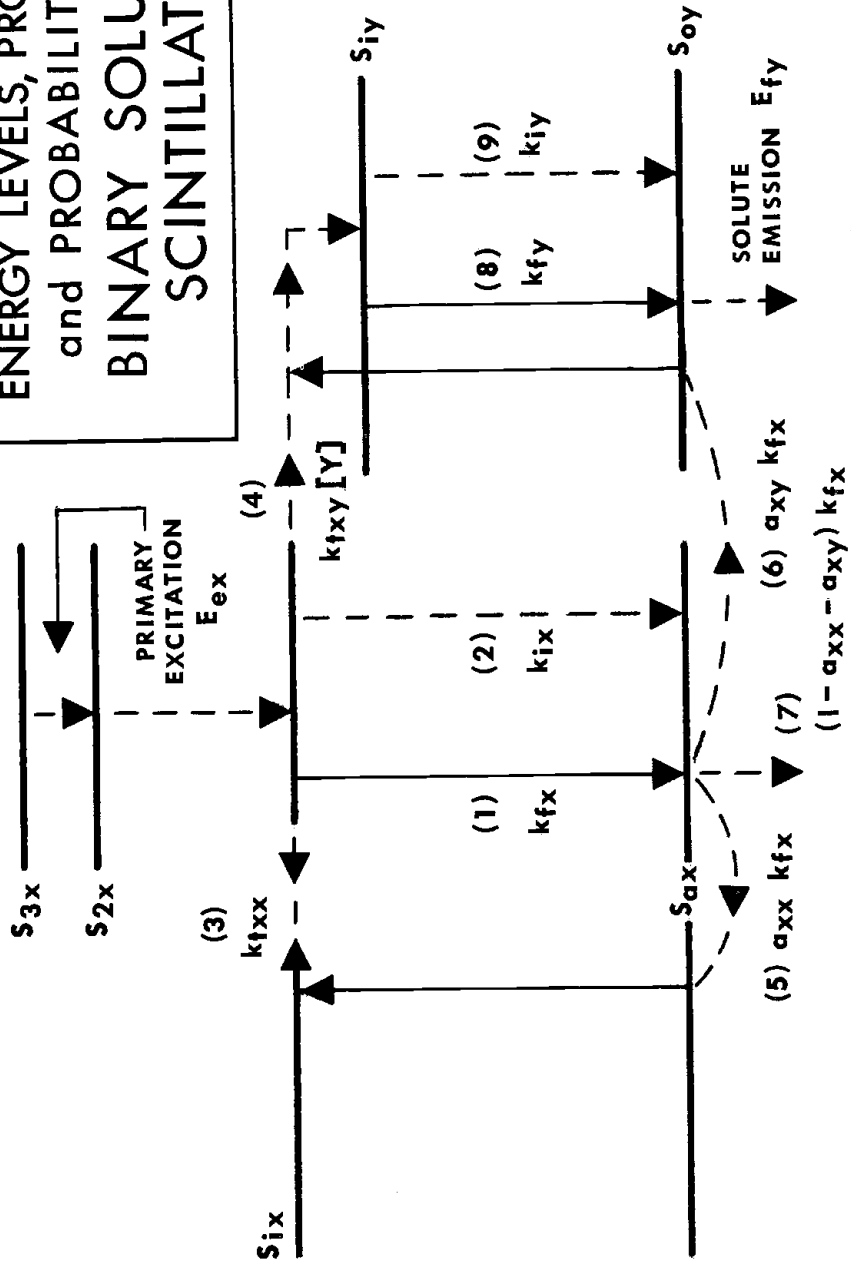
$$a_{xy} = 1 - \exp(-\epsilon_{xy}[Y]d) \quad (5)$$

where  $\epsilon_{xy}$  is the extinction coefficient, in appropriate molecular units of Y averaged over the emission spectrum of X, and  $d$  is the thickness. The quantity  $a_{xy}$  tends to unity as [Y] or  $d$  is increased. In scintillator solutions of normal size,  $a_{yy}$  (self-absorption of primary solute emission) is negligible.

The processes competing for the  $S_{ix}$  excitation energy in a binary solution scintillator are as follows (Figure 2):

**ENERGY LEVELS, PROCESSES,  
and PROBABILITIES in  
BINARY SOLUTION  
SCINTILLATOR**

FIGURE 2



- (1) Solvent emission,  $k_{fx}$ ;
- (2) Internal quenching of solvent,  $k_{ix}$ ;
- (3) Non-radiative migration to solvent,  $k_{txx}$ ;
- (4) Non-radiative transfer to primary solute,  $k_{txy}[Y]$ ;
- (5) Radiative migration to solvent,  $a_{xx}k_{fx}$ ;
- (6) Radiative transfer to primary solute,  $a_{xy}k_{fx}$ ; and
- (7) Escape of solvent emission  $(1 - a_{xx} - a_{xy})k_{fx}$ .

The importance of process (3) is that, by increasing the mobility of the solvent excitation energy, it enhances the efficiency of non-radiative transfer. In a liquid system, where the molecules are mobile, molecular diffusion (Brownian motion) similarly increases the efficiency of process (4).

In the usual liquid or plastic solvents, radiative migration, process (5), is generally negligible, so that  $a_{xx} = 0$ . In mixed crystals, e.g. naphthacene in anthracene,  $a_{xx}$  cannot however be neglected, and radiative migration has been shown to influence the technical efficiency of both radiative and non-radiative transfer (1, 11). The case of  $a_{xx} \neq 0$  has been treated in detail previously (1), and hence only the case of  $a_{xx} = 0$ , which is of practical interest for liquid and plastic scintillators, will be considered here.

In the presence of Y, the molecular fluorescence quantum efficiency of X is reduced to

$$q_{ox} = \frac{k_{fx}}{k_{fx} + k_{ix} + k_{txy}[Y]} \quad (6)$$

The technical fluorescence quantum efficiency (escape of emission) of X is, for  $a_{xx} = 0$

$$q_{px} = q_{ox}(1 - a_{xy}) \quad (7)$$

The technical quantum efficiency of radiative transfer to Y is

$$\eta_r = q_{ox} a_{xy} \quad (8)$$

and the technical quantum efficiency of non-radiative transfer is

$$\eta_t = \frac{k_{txy}[Y]}{k_{fx} + k_{ix} + k_{txy}[Y]} \quad (9)$$

Thus the total quantum efficiency of energy transfer from X to Y is

$$\begin{aligned} \eta_{xy} &= \eta_r + \eta_t \\ &= \frac{(q_{ox})_0 a_{xy} + \sigma_{xy}[Y]}{1 + \sigma_{xy}[Y]} \end{aligned} \quad (10)$$

where  $(q_{ox})_0$  is the molecular quantum efficiency of X for  $[Y] \neq 0$ , and

$$\sigma_{xy} = \frac{k_{txy}}{k_{fx} + k_{ix}} \quad (11)$$

The excitation energy transferred to Y by processes (4) or (6) is "trapped", the excess vibrational energy being rapidly dissipated thermally yielding a molecule with  $S_{iy}$  excitation energy. The two processes competing for this energy ( $a_{yy} = 0$ ) are (Figure 2),

- (8) Primary solute emission,  $k_{fy}$ , and
- (9) Internal quenching,  $k_{iy}$ .

The molecular quantum efficiency of fluorescence of Y is

$$q_{oy} = \frac{k_{fy}}{k_{fy} + k_{iy}} \quad (12)$$

Hence the overall energy conversion efficiency from the primary excitation of X to the fluorescence emission of Y is

$$\begin{aligned}
 Q &= \frac{E_{fy}}{E_{ex}} \eta_{xy} q_{oy} \\
 &= \frac{\lambda_{ex}}{\lambda_{fy}} \eta_{xy} q_{oy} \quad (13)
 \end{aligned}$$

where  $E_{ex}$  and  $E_{fy}$  are the mean energies of the primary excitation of the solvent and the fluorescence emission of the solute respectively, obtainable from  $\lambda_{ex}$  and  $\lambda_{fy}$ , the mean wavelengths of the absorption spectrum of the solvent and of the emission spectrum of the solute respectively.

The dependence of  $\eta_{xy}$  on  $[Y]$  has been studied using either ionizing radiation or ultra-violet radiation for excitation of the fluorescence. The former method yields relative values only, i.e.  $S$  is measured in arbitrary units as a function of  $[Y]$ , the other factors in equations (1) and (13) not being evaluated. With ultra-violet excitation the intensity  $I$  of the solute fluorescence excited indirectly by solvent absorption can be compared with that excited directly by solute absorption, and the absolute value of  $\eta_{xy}$  is determined directly from the ratio (12,13,14). The quantities  $S$  and  $I$  have been shown to depend in a similar manner on  $[Y]$ , as predicted by the theory (15).

The dependence of  $\eta_{xy}$  on concentration in a typical plastic solution, TPB in polystyrene of 1 cm. thickness, as evaluated from combined experimental data on  $I$  (14) and  $S$  (16), is shown in Figure 3. The concentration is expressed in moles/liter, which is approximately 10  $[Y]$  if the styrene molecule is taken as the solvent molecular unit. At low concentrations the energy transfer is purely radiative, increasing to a maximum of  $\eta_r \sim (q_{ox})_0$  at about  $5 \times 10^{-4} M$ . Non-radiative transfer becomes significant about  $10^{-4} M$ , and as the concentration is increased it competes with the internal quenching and the emission, hence causing a decrease in  $\eta_r$ , and it becomes predominant at high concentrations, where  $\eta_t$  tends towards unity.

Practical plastic and liquid solution scintillators

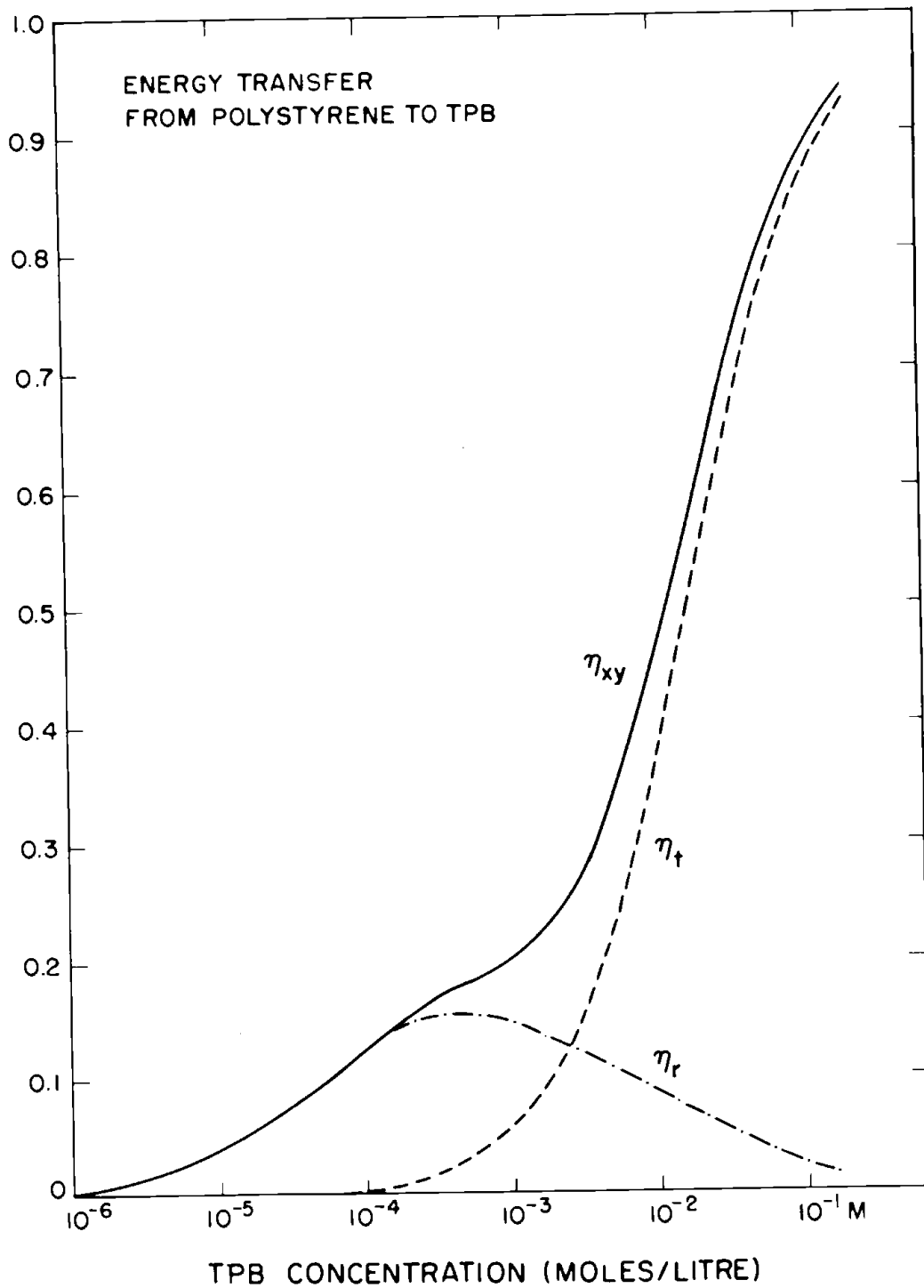


Fig. 3. Solvent-solute transfer in plastics.

utilize high solute concentrations since thereby  $\eta_{xy}$  and  $S$  are maximized, while the scintillation decay time is minimized towards the fluorescence decay time of the solute alone. Two factors limit the maximum concentration that can be used, and hence reduce the practical value of  $\eta_{xy}$  below the theoretical maximum of unity. These are (a) the maximum solubility, and (b) the concentration quenching effect by which the solute fluorescence efficiency  $q_{oy}$  is reduced by solute-solute interaction at high  $[Y]$ . Due to the latter effect  $\eta_{xy}q_{oy}$  may decrease as  $[Y]$  is increased, so that the optimum concentration is that at which  $\eta_{xy}q_{oy}$  is a maximum [equation (13)].

The dependence of  $\eta_{xy}$  on concentration in a typical liquid solution, *p*-terphenyl in toluene, as evaluated from experimental data on I (12,15,19), is shown in Figure 4. Here the radiative component  $\eta_r$  is negligible because of the low fluorescence efficiency  $(q_{ox})_0$  of the pure liquid solvent. As before,  $\eta_t$  tends towards unity at high concentration, the maximum being limited by the solubility, but it is noteworthy that the non-radiative transfer occurs efficiently at lower concentrations than in plastic solutions, corresponding to a higher value of  $\sigma_{xy}$ .

Since  $(k_{fx} + k_{ix})^{-1}$  in equation (11), which is equal to the solvent fluorescence decay time, is 14 n sec. for polystyrene and 7.5 n sec. for toluene, it follows that  $k_{txy}$  is significantly greater for a liquid solution than for a plastic solution. The  $k_{txy}$  value for polystyrene-TPB agrees well with the dipole-dipole transfer probability between static molecules calculated from Förster's theory (17), indicating that non-radiative migration is relatively unimportant in plastic solutions. The non-exponential scintillation decay of plastic scintillators (18), and the observed dependence (16) of  $\sigma_{xy}$  on  $\sqrt{J_{xy}}$  for a wide range of solutes, where  $J_{xy}$  is the Förster overlap integral, are also consistent with relative immobility of the solvent excitation energy in plastic solutions, and with dipole-dipole non-radiative transfer (single-step). An approximate calculation based on the rather limited data on the overlap of the absorption and emission spectra of polystyrene

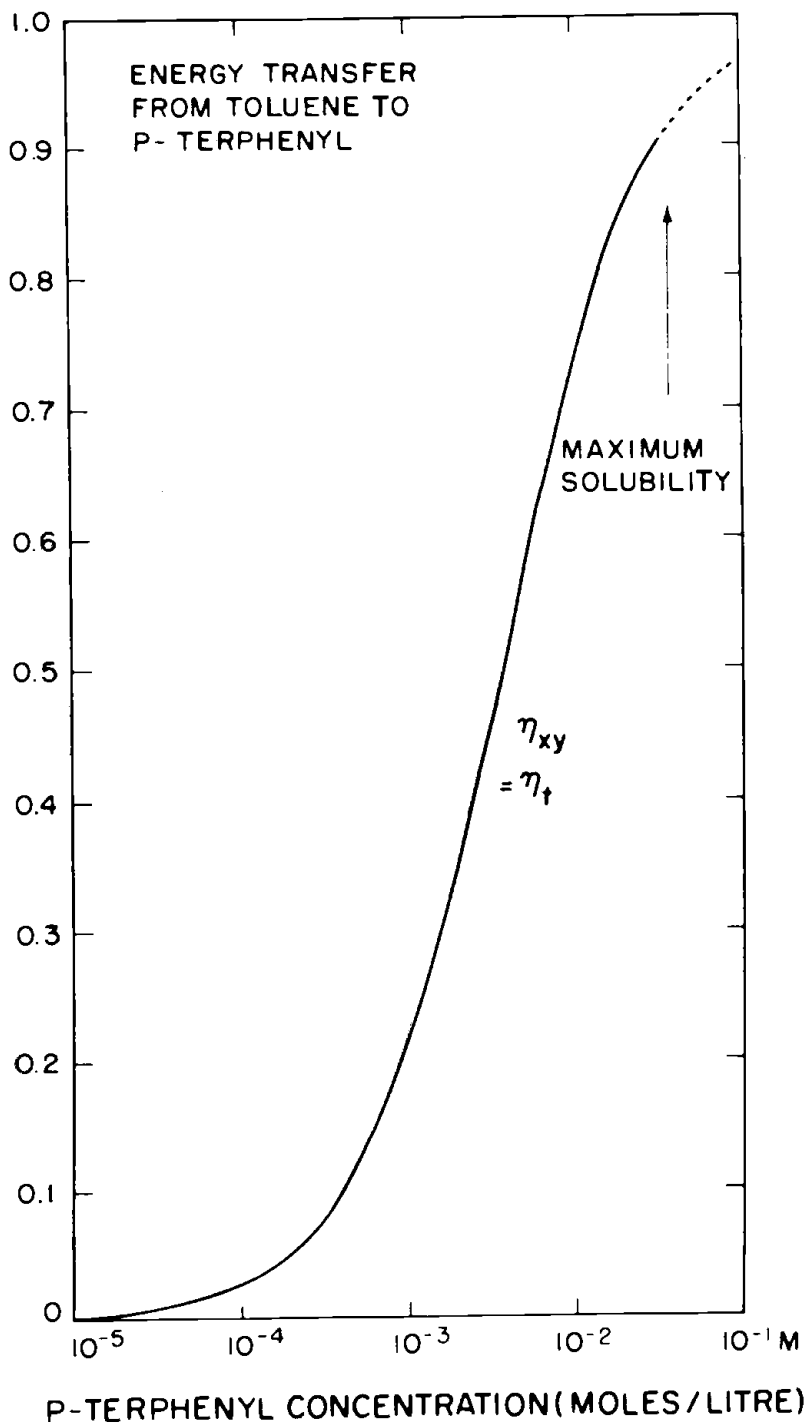


Fig. 4. Solvent-solute transfer in liquids.

indicates that the critical Förster dipole-dipole migration distance in polystyrene is probably less than  $6.6 \text{ \AA}$ , the average spacing between the phenyl groups in the polymer chain, thus indicating why the migration process is inefficient.

In liquid solutions  $k_{txy}$  is much greater than is to be expected for single-step dipole-dipole transfer. Thus for p-terphenyl in toluene (12),  $k_{txy}$  corresponds to a critical transfer distance of  $38 \text{ \AA}$ , which is equivalent to a transfer distance of  $27 \text{ \AA}$  between static molecules, when the molecular diffusion is allowed for. This exceeds the theoretical value of  $15 \text{ \AA}$ , indicating that non-radiative migration must also occur and contribute to the transfer efficiency.

Earlier measurements by Birks and Cameron (13) on terphenyl-toluene solutions indicated that  $\eta_{xy}$  varied with the wavelength of the ultra-violet excitation of the solvent, suggesting energy transfer from  $S_{2x}$  in competition with internal conversion to  $S_{ix}$ , and that  $\eta_{xy}$  tended to a maximum value less than unity as the concentration increased, which was attributed to quenching of the solvent excitation by the solute. These results were at variance with those of Cohen and Weinreb (12) quoted above. A detailed investigation (19) has been made of the cause of the discrepancy, which is found to have been due to the use of a broad divergent light beam for excitation. As the size of the illumination area is reduced, the observed wavelength variation of  $\eta_{xy}$  is correspondingly reduced. For a spot size of 1 mm. diameter and terphenyl-toluene solutions of 5 different concentrations,  $\eta_{xy}$  is found to vary by not more than  $\pm 4$  per cent, for excitation wavelengths from  $2200 \text{ \AA}$  to  $2700 \text{ \AA}$ . This result compares with the  $\pm 5$  per cent variation observed by Cohen and Weinreb (12) and confirms their conclusion that  $\eta_{xy}$  is independent of wavelength in this spectral range. It is also found in agreement with their results that  $\eta_{xy}$  has a limiting value of 1.0.

### 3.4. Ternary Solutions.

The processes that compete in the transfer of the primary excitation energy  $E_{\text{ex}}$  of the solvent X, through the  $S_{1Y}$  excitation energy of the primary solute Y, to the  $S_{1Z}$  excitation of a secondary solute Z are shown diagrammatically in Figure 5. The competing processes in the energy transfer from Y to Z are similar to those considered in solvent-solute transfer in Section 3.3. Equations (6) to (12) are directly applicable, substituting Y for X and Z for Y throughout.

The overall energy conversion efficiency from the primary excitation of X to the emission of Z is

$$Q = \frac{\lambda_{\text{ex}}}{\lambda_{\text{fz}}} \eta_{\text{xy}} \eta_{\text{yz}} q_{\text{oz}} \quad (14)$$

where  $q_{\text{oz}}$  is the molecular fluorescence quantum efficiency of Z,  $\eta_{\text{yz}}$  is the total quantum efficiency of energy transfer from Y to Z, and  $\lambda_{\text{fz}}$  is the mean wavelength of the emission spectrum of Z.

Recent studies (19) have been made of the energy transfer from *p*-terphenyl to TPB in toluene solutions, TPB being chosen as the secondary solute because its emission can be separated from that of terphenyl with suitable filters. The quantity  $\eta_{\text{yz}}$  was determined as a function of [Z] from the ratio of the TPB emission excited by indirect terphenyl absorption and direct TPB absorption respectively. In addition the terphenyl emission intensity was measured as a function of [Z]. The results for solutions of 1.3 cm. thickness, which have been analyzed in terms of equation (10) are plotted in Figure 6. Up to TPB concentrations of  $10^{-4}$  M, the energy transfer is primarily radiative, and both the TPB and terphenyl emission intensities are found to depend on the solution thickness [equation (5)]. The molecular fluorescence quantum efficiency  $q_{\text{oy}}$  of *p*-terphenyl is observed to be 0.75. Above  $10^{-4}$  M, the terphenyl emission is suppressed, and non-radiative transfer becomes important, increasing toward unit quantum efficiency as the concentration is increased. These

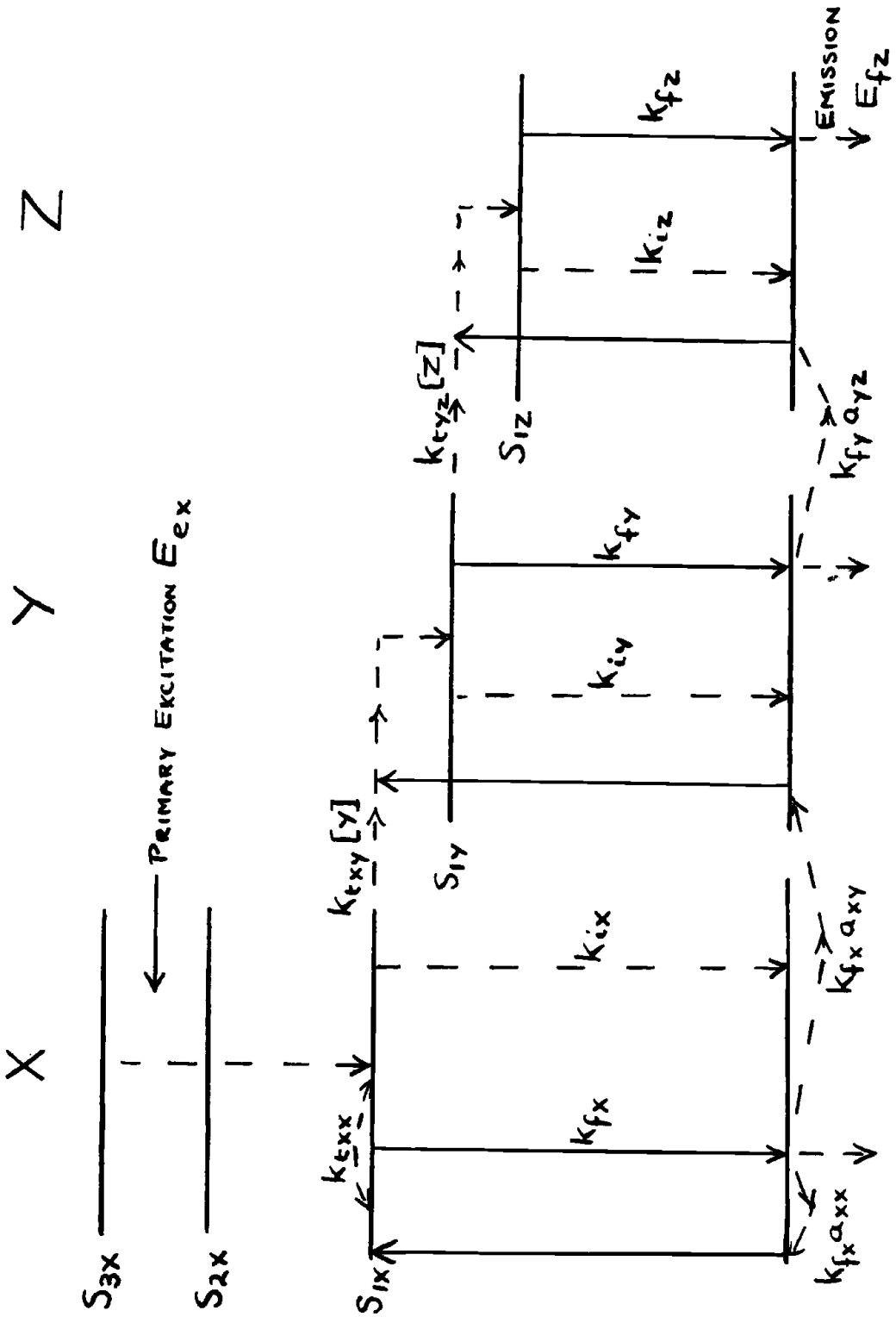


Fig. 5. Energy levels, processes, and probabilities in ternary solution scintillator.

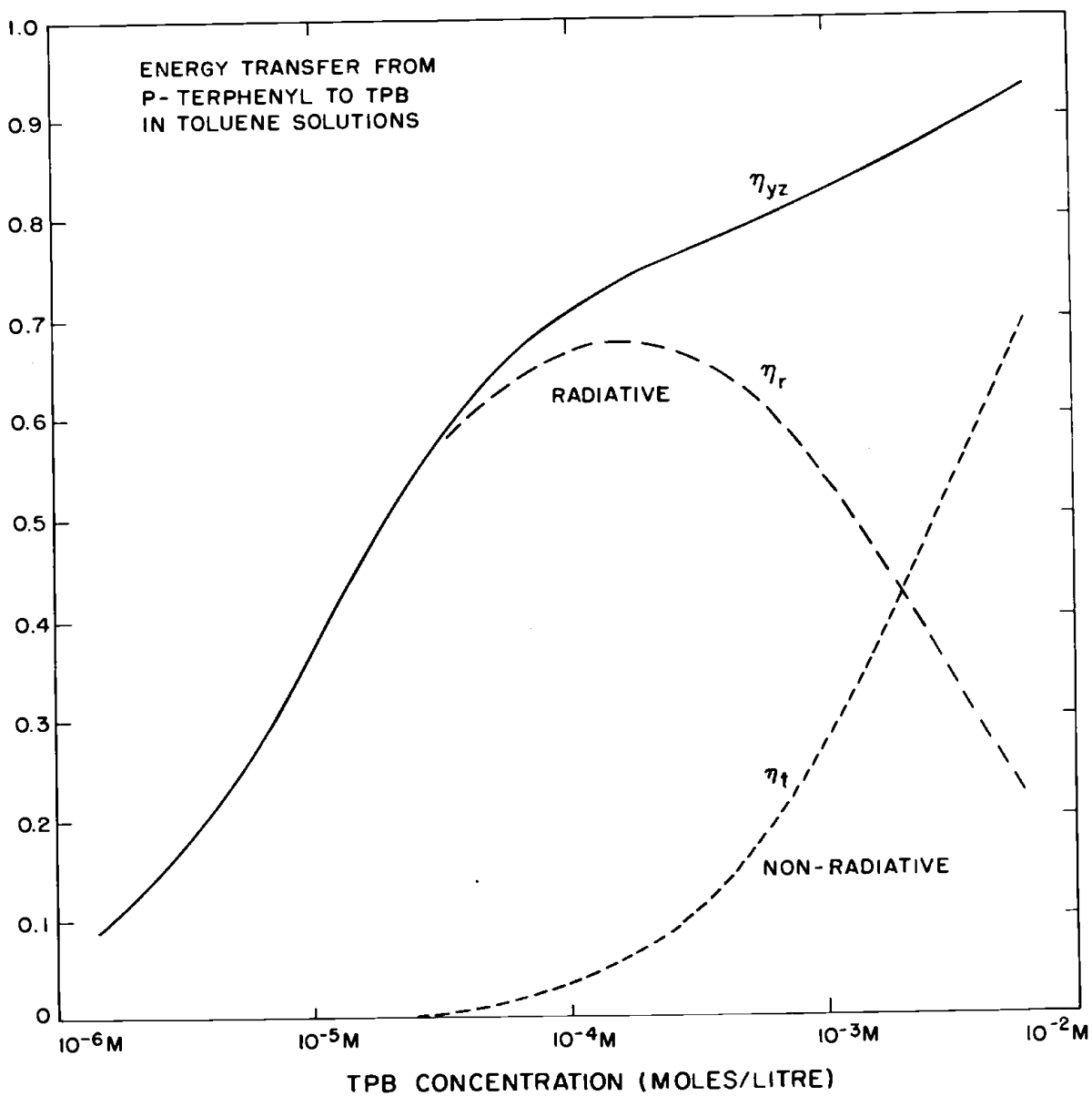


Fig. 6. Energy transfer from primary to secondary solute.

results which throw an interesting light on the mode of operation of secondary solutes will be reported in more detail elsewhere.

#### 4. SCINTILLATION EFFICIENCY.

The basic equation for the scintillation efficiency is

$$S = PQ \quad (1)$$

where, on the simple theory proposed,

$$P = 2/3 \text{ (the } \pi\text{-electron fraction of solvent)} \quad (1a)$$

and Q is given by equations (4), (13) and (14) for pure crystals, binary solutions, and ternary solutions respectively.

The term P has a similar value of about 0.1 for the better crystals and liquid solvents (Table 1). It is inherently lower for a plastic solvent, though it can be improved by introducing larger aromatic substituents in the polymer chain to increase the  $\pi$ -electron fraction.

Considering now the factors influencing Q, the transfer efficiencies  $\eta_{xy}$  and  $\eta_{yz}$  in solution scintillators can be made to approach unity by the use of sufficiently high solute concentrations. Two factors limit the maximum  $\eta$  that can be achieved in practice: the maximum solubility of the solute in the solvent; and concentration quenching which becomes important with some solutes at high [Y] and reduces  $q_{oy}$ . Pure crystal scintillators have the advantage that no solvent-solute transfer processes are involved.

The requirements for the final emitting molecule in the system are that it should have a high fluorescence quantum efficiency, and that its emission should match the photo-multiplier spectral response. Crystalline anthracene satisfies the latter requirement, although its quantum efficiency is reduced from  $q_o = 0.9$  to  $q_p = 0.62$  by self-absorption, yielding  $S = 0.037$ . If self-absorption were eliminated, i.e. for a thin anthracene crystal at 290°K,

we would obtain  $S = 0.054$ . Alternatively self-absorption and internal quenching can be reduced by cooling the crystal, thereby increasing  $S$ . Data on the variation of  $S$  for anthracene with temperature have been presented elsewhere (1). At  $0^\circ\text{K}$  with  $q_p = 1.0$ , we obtain  $S = 0.06$ . This corresponds to about the maximum theoretical scintillation efficiency attainable with any organic scintillator, since  $P$  is about the optimum and the ratio  $\lambda_e/\lambda_f$  is about the same for all aromatic molecules.

It is of interest to note that the absolute scintillation efficiency of crystalline *p*-terphenyl at room temperature is probably higher than that of crystalline anthracene. It has similar values of  $P$  and  $\lambda_e/\lambda_f$ , with negligible self-absorption and  $q_p \sim 0.65$ . Its emission is, however, in the near ultra-violet and matches the blue-green photo-multiplier response imperfectly, so that its practical efficiency is inferior to that of anthracene.

Similarly *p*-terphenyl has a high  $q_0 = 0.75$  in liquid solution and a similar value in plastic solution, but secondary solutes, chosen also to have a high  $q_0$ , are required to "shift" the emission to match the multiplier response, with a resultant decrease in the absolute scintillation efficiency  $S$  due to the further energy degradation from  $S_{iy}$  to  $S_{iz}$ , but with a gain in practical efficiency. The development of photo-multiplier with a sensitivity in the near ultra-violet comparable with the existing blue-green sensitivity would eliminate the need for secondary solute wavelength-shifters, and would properly utilize the high absolute scintillation efficiency of *p*-terphenyl in the crystalline and liquid and plastic solution phases.

With the optimum  $\lambda_f$  dictated at present by the photo-multiplier response, it is important for  $\lambda_e$  to be as large as possible. The fraction  $\lambda_e/\lambda_f \sim 0.6$  is about the same for all aromatic molecules, due to the interdependence of the  $\pi$ -electron singlet energy levels. Hence the largest value of  $\lambda_e \sim 2500 \text{ \AA}$  (consistent with  $\lambda_f \sim 4200 \text{ \AA}$ ) is obtained in a single component scintillator like anthracene. The usual liquid and plastic solvents have  $\lambda_e$  in the region of  $1500\text{-}2000 \text{ \AA}$ , corresponding to only  $0.6\text{-}0.8$  of that of

anthracene. It is of interest to note that this approximates to the range of relative scintillation efficiencies attainable, indicating that apart from  $\eta$ ,  $\lambda_e$  is the main factor limiting the performance of solution scintillators. Data on the absorption spectra in the vacuum ultra-violet region are sparse, except for the simpler liquid solvents, but since  $\lambda_e \sim 0.6 \lambda_f$ ,  $\lambda_e$  can be estimated from the solvent  $\lambda_f$ . Thus for benzene  $\lambda_e \sim 1600 \text{ \AA}$ , and for polystyrene  $\lambda_e \sim 1850 \text{ \AA}$ . The quantity  $\lambda_e$  can be increased by using liquid or plastic solvents having larger molecules or monomer units, preferably containing more than one benzene ring (e.g. polyvinyl-naphthalene) or having suitable substituents which shift with the absorption spectrum to longer wavelengths. With improved solvents the trend should preferably be towards binary solutions, to eliminate one energy transfer process, except where primary solute self-absorption or economic factors are important.

One early binary solution system which merits reconsideration is anthracene in naphthalene (20). These mixed crystals have  $P = 0.1$ ,  $\lambda_{ex} \sim 2100 \text{ \AA}$ ,  $\lambda_{fy} = 4200 \text{ \AA}$ ,  $q_{oy} = 0.9$ , so that if  $\eta_{xy} = 1$  can be achieved, we obtain  $S = 0.045$ , i.e. a scintillation efficiency about 20 per cent greater than pure anthracene, with an emission matching the photomultiplier response.

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